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(54) SENSITIZING SOLUTIONS FOR ELECTROLESS PLATING AND METHODS FOR THE MANUFACTURE AND USE OF SAME

(71) We, KOLLMORGEN CORPORATION, Glen Cove, United States of America, a Corporation organized and existing under the Laws of the State of New York, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to new and useful precious metal sensitizing solutions. More particularly the invention relates to solutions comprising a precious metal complex, and to concentrates thereof. The solutions are used to render surfaces of a substrate catalytic to the uniform reception and deposition thereon of metal without resort to an external source of electricity. The electroless deposition of a metal on either a metallic or non-metallic substrate usually requires pretreatment or sensitization of the substrate to render it catalytic to the reception of such deposit. Various methods have evolved over the years employing particular sensitizing compositions.

One of the earliest innovations employed a plurality of baths in which the substrate was subjected to a basic two-step process entailing, e.g., immersion in a stannous chloride solution, followed by immersion in an acid palladium chloride solution. More recently, there has also been proposed a unitary treating process employing only one bath solution. The plural bath process while readily effecting sensitization is rather complicated and further produces an undesired precious metal flash coating. Known unitary bath processes, while overcoming the flash coating problem tend to produce diminished catalytic reactivity.

Accordingly, it is a primary object of the present invention to provide a new sensitizer composition, and stable concentrates thereof, dilutable to highly active sensitizers, as well as a new process to effect the sensitization of a substrate to render it catalytic to the reception of an electroless metal deposit.

[Price 25p]

Another object of the present invention is to provide new and useful stabilized compositions which are true solutions.

It is an additional object of the invention to provide clear, stable compositions which are true solutions, and dilutable concentrates therefor and processes for the use thereof which materially reduce the time necessary to effect sensitization.

Yet another object of the invention is to provide dilutable, concentrated compositions and methods for sensitizing substrates with a precious metal complex which involve using very dilute treating solutions and thereby materially diminishing production costs.

The sensitizing solutions of this invention comprise a solution of a double metal complex consisting of three components:

- a precious metal selected from the metals of the fifth and sixth periods of Groups VIII and IB of the periodic table of elements;
- a Group metal of the periodic table of elements which is capable of two valence states; and
- an anion capable of forming a stable moiety with both valence states of the Group IV metal, the molar ratio of components (a) to (b) to (c) being 1:1:3 to 1:6:24;

the said double metal complex having been formed by heating the mixture containing said components (a), (b) and (c) for a period of time which is sufficient for forming it.

It is a further object of the invention to prepare the said solution in concentrated form and to dilute it for use. In such case concentration of component (a) is preferably at least 1.5 grams/liter.

A preferred embodiment of the invention is a stabilized sensitizing solution as above defined which includes as the stabilizer an organic mono-ol, diol or polyol, i.e., mono-hydroxy, dihydroxy and polyhydroxy organic compounds, the amount of said compound in said solution being at least sufficient to prevent

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separation therefrom of component (a) as a metallic film or precipitate.

Also contemplated are optically-clear sensitizing solutions which have been prepared by diluting the concentrates with water, an acid or a mixture of water and an acid, until the concentration of component (a) has been reduced to from about 0.0005 grams/liter to about 2.5 grams/liter.

Another feature of the invention is a process to prepare the concentrate comprising heating an aqueous mixture of the components (a), (b) and (c) at a suitable temperature of, e.g., from 80°C to the boiling point, until formation of the complex is complete.

Still another feature is a process to prepare the concentrate which comprises mixing an aqueous solution of components (a) and (c) with an aqueous solution of components (b) and (c) and heating the mixture at from 80°C. to its boiling point.

The present invention further relates to an improved process for rendering surfaces receptive to the deposition of an adherent electrolessly formed metal deposit, as well as a process for electrolessly depositing a metal on a substrate which has been sensitized with the sensitizing solutions of the present invention.

An additional embodiment of the invention relates to particular acidic precious metal solutions for rendering surfaces receptive to the deposition of electroless copper.

An advantage of the present invention is that sensitization as taught herein leads to practically complete avoidance of the deposition of a flash coating of precious metal from the sensitizing bath. A flash coating of precious metal normally leads to a low grade of adhesion. Also, avoidance of such deposition economically conserves the precious metal.

Yet another advantage of the present invention is realized in manufacturing presensitized plastic base members. In essence, the sensitizing solution can be directly incorporated in a plastic base at the time of its manufacture. This can be achieved by utilizing an organic sensitizing solution employing a solvent such as cyclohexanone, or a highly viscous paste like composition. Alternatively, the solution can be reduced to a solid form by employing a counter ion and directly incorporating such solid in a plastic base at the time of manufacture. Therefore, the advent of the present invention provides for the preparation of presensitized plastic solutions. In essence, a complex is formed between the metals and the anion. The preferred palladium - tin - chloride complex of this invention, for example, in addition to being acid soluble, is soluble in organic solvents, e.g., dimethylformamide; cyclohexanone hexane, dimethyl sulfoxide, and the like. It is optically clear in dilute solution. It is filterable through ultra-membranes through which colloidal sensitizing

suspensions will not pass. The said complex has been found to have an ultraviolet absorption peak at 395 m μ . Once formed, concentrates of the complex according to this invention, may be diluted to levels of concentration which cannot easily and reproducibly be directly formulated in active sensitizing solutions.

The treating of sensitization procedure which is an embodiment of this invention is an intermediate step between pretreatment or cleaning of the surfaces upon which the metal is to be electrolessly deposited and the actual deposition of the metal.

The sensitizing solution comprises an aqueous solution of a metal complex as defined above consisting of (a) a precious metal, (b) a Group IV metal and (c) an anion. It is optically-clear, i.e., non-colloidal. Among the precious metals that may be mentioned are palladium, platinum, gold, rhodium, osmium, iridium and mixtures of these metals. The inorganic and organic acid salts of these metals, and of the Group IV metals, such as the chlorides, bromides, fluorides, fluoborates, iodides, nitrates, sulfates and acetates of stannous tin, titanium and germanium among others may be used. Other acid salts of the precious metals and Group IV metals will readily suggest themselves to those skilled in the art.

The concentration of the precious metal ion in the concentrates will preferably be at least 1.5 grams/liter. The upper practical limit will be about 100 grams/liter. In the sensitizing solution bath the precious metal concentration should preferably be from at least about 0.0005 to 1.5 grams/liter of solution. The sensitizing bath solution can be prepared directly or by diluting a concentrate.

The sensitizing solutions or concentrates are prepared by heating the salts of the precious metals and a Group IV metal salt in an aqueous acidic solution as will be described hereinafter. Among the acids that may be mentioned are hydrochloric acid, hydrofluoric acid, fluoboric acid, hydroiodic acid, sulfuric acid and acetic acid. Preferably, the anion of the organic acid corresponds to the anion of the salt of the precious metals, or to the anion of the Group IV metal salt. Where the anions of the precious metal salt and the Group IV metal salt are the same, the anion of the acid should preferably correspond to the common anion of the salts. Where the anion of the precious metal differs from that of the Group IV metal salt, the anion of the acid preferably corresponds to the anion of the precious metal salt. However, acids having anions which differ from the anions of the precious metal salts or of the Group IV metal salt may also be used. Preferred anions are Cl⁻ and SnCl₃⁻.

The concentration of the acid in the sensitizing solutions and in the concentrates

depends upon the strength of the acid employed. The concentration of the acid in the final solution should be at least 0.001 Normal. At the upper end, especially in the concentrate the concentration of acid may be as high as 15 Normal, or even higher. When strong acids are used, the concentration of the acid in the sensitizing solution generally varies between about 0.02 and 7.5 Normal. When weak acids are used, the concentration of the acid in the sensitizing solution approaches the upper limit given hereinabove.

The Group IV metal ion concentration may vary widely but must be maintained in excess of a stoichiometric amount based on the amount of precious metal ions present in the sensitizing solution. Normally a large excess of, for example, stannous chloride is maintained to allow for air oxidation of the stannous ion. Illustratively, concentrations of as high as 50 grams per liter of stannous chloride are not detrimental to the effectiveness of the sensitizing activity of the diluted solutions.

The sensitizing solutions and concentrates thereof, of the present invention may contain additional agents to stabilize the solution, e.g., against the effects of atmospheric oxidation. Such agents will include the use of additional quantities of the Group IV metal, as for example, additional stannous chloride may be added to a palladium, stannous chloride sensitizing solution; other useful stabilizing agents are the fluorinated hydrocarbons.

As has been mentioned above, addition of an organic mono-ol, diol or polyol to the sensitizing solutions of this invention improves the stability of the solutions and avoids formation of precious metal residues on surfaces, e.g., metal surfaces, exposed to such solutions.

Baths to which an effective amount of the stabilizing ingredients has been added will remain clear and be stable over extended periods of storage and use. The compounds which can be used most efficiently are relatively low molecular weight, polysubstituted ones with hydroxy groups or containing at least one hydroxy group and other functional groups such as sulfonic acid groups, phosphate groups, amino groups, halogens, carboxyl groups, which tend to enhance solubility in polar media.

Preferred stabilizing ingredients are open chain aliphatic mono-ols, diols or polyols of from about 1 to about 12 carbon atoms, e.g., methanol, ethanol, *i*-propanol, ethylene glycol, propylene glycol, 1,4-butane diol, glycerol, glucose, sucrose, and the like; and closed chain aliphatic or aromatic mono- or di-carbocyclic mono-ols, diols or polyols of from about 6 to about 12 carbon atoms, e.g., cyclohexanol, cyclohexanediol, inositol, phenol, β -naphthol, resorcinol, catechol, hydroquinone, pyrogallol,

phloroglucinol, naphthoresorcinol, and the like.

It is preferred that the stabilizing ingredients have a water solubility of at least greater than about 4% by weight, especially those in the aromatic family. Particularly preferred stabilizing ingredients are isopropanol, ethylene glycol, glycerol, resorcinol, catechol, hydroquinone, pyrogallol and phloroglucinol. These can generally be employed at an appropriate concentration in the range of from about 2 to about 50% by weight in the final mixture. The aromatic compounds will be employed at 2 to 7 wt.% and the aliphatic compounds will be used in concentrations of from about 4 to 50 wt.%, although higher and lower amounts can be formulated, as mentioned above. An especially preferred stabilizer is resorcinol at 20 to 70 grams/liter.

While it should not be construed as limiting the invention, it is believed that the complexing reaction which occurs between the metals and the anion results in the formation of more than one and possibly several complexes. In the case of Sn and Cl these can be, empirically, depicted as including complex anions of the formulae



mixtures thereof, wherein Me is Ru, Rh, Pd, Os, Ir, Pt, Au or a mixture thereof.

The concentrations of the components of the complex are expressed in terms of molar ratio. Therefore, the molar ratio of precious metal to Group IV metal to anion is from 1:1:3 to 1:6:24.

The concentrates of this invention can be prepared by so-called one-step and two-step processes. In the first, an aqueous mixture is heated, which contains components (a), (b) and (c), as defined above—with component (a) preferably being present in a concentration of at least 1.5 grams/liter—; at a temperature of from, e.g., 80°C to the boiling point of the mixture until formation of the metal complex is substantially complete. In a so-called two-step process, there is provided an aqueous solution containing a salt of component (a) in a concentration of from, e.g. 1.5 grams/liter up to about the limit of solubility of the salt in water at the boiling point and component (c); and an aqueous solution of components (b) and (c), the ratios of (a):(b):(c) being 1: at least 1: at least 3. The two solutions are mixed and heated at a temperature of from, e.g., 80°C to the boiling point of the mixture until formation of the complex is substantially complete. With pal-

ladium concentrations of, e.g., 8 to 100 grams/liter (calculated as metal) can be conveniently used. Depending on the temperature, it is preferred to heat from about 20 to 90 minutes, although this is not critical.

The following examples are provided for illustrative purposes and may include particular features of the invention. However, the examples should not be construed as limiting the invention, many variations of which are possible without departing from the scope thereof.

EXAMPLE 1

A stable, concentrated composition, dilutable to an optically clear, sensitizing solution is prepared as follows:

A first solution is prepared comprising the following ingredients:

	palladium chloride (g.)	62.9
	hydrochloric acid (37%, ml.)	200
	water to make total (ml.)	500

A second solution is prepared comprising the following ingredients:

	stannous chloride dihydrate	800 grams
	hydrochloric acid (37%)	500 ml

The first solution is added to the second with agitation and the mixture is heated to 85°C. and then boiled in a well ventilated place for one hour.

The mixture is allowed to cool and there is obtained a concentrate according to this invention, which contains palladium in a concentration of about 50 grams/liter.

EXAMPLE 2

Stable, concentrated compositions, dilutable to optically-clear sensitizing solutions are prepared, according to Example 1.

The first solutions comprise, respectively:

	palladium chloride (g.)	3.10	93.25	125
	hydrochloric acid (37%) (ml.)	200	200	200
	water to make (ml.)	500	500	500

The second solution is the same as that in Example 1. There are obtained concentrates according to this invention, which contain palladium in concentrations, respectively, of about 2.5, 75 and 100 grams/liter.

EXAMPLE 3

A stable, concentrated composition, dilutable to an optically-clear sensitizing solution is prepared in one step. The following formulation is used:

	palladium chloride (g.)	62.5
	hydrochloric acid (37%)(ml.)	700
	stannous chloride dihydrate (g.)	800
	water to make total (ml.)	1295

Stannous chloride is dissolved in the hydrochloric acid. The palladium chloride is added with agitation. Then the water is added and the mixture is heated to 85°C. for 20 minutes, then boiled for 1.5 hours and cooled.

There is obtained a concentrate according to the invention which contains about 50 grams/liter of palladium.

EXAMPLE 4

A first solution is prepared comprising the following ingredients

	palladium chloride (g.)	10
	hydrochloric acid (37%, ml.)	200
	water to make total (ml.)	500

The palladium salt dissolves slowly in the acid-water mixture.

A second solution is prepared comprising the following ingredients:

	stannous chloride dihydrate (g.)	800
	hydrochloric acid (37%, ml.)	500

The first solution is added to the second with agitation, then the mixture is boiled for 1.5 hours, during which time it changes color from straw-yellow, through brown to blue or purple.

The mixture is allowed to cool and there is obtained a concentrate according to this invention which contains palladium in a concentration of about 8 grams/liter.

EXAMPLE 5

The procedure of Example 1 is repeated, respectively substituting for the palladium chloride, stoichiometrically-equivalent amounts of the following: ruthenium chloride (RuCl_3); rhodium chloride (RhCl_3); osmium chloride (OsCl_4); iridium chloride (IrCl_3); and platinum chloride (PtCl_4). Concentrates according to this invention containing, respectively, about 50 grams/liter of ruthenium, rhodium, osmium, iridium and platinum are obtained.

EXAMPLE 6

A sensitizing solution according to this invention is prepared by taking 20 ml. of the concentrate from Example 1, diluting it with a mixture comprising 490 ml. of 37 per cent hydrochloric acid and 490 ml. of water. The resulting solution will contain about 1 gram/liter of palladium in the form of the palladium-stannous chloride complex of this invention and will have good catalytic activity.

In a similar manner, catalytically active sensitizing solutions according to this invention are prepared by taking 0.01 ml. and 50 ml. portions of the concentrate of Example 1 and diluting them, respectively, to 1 liter in 1:1 by volume of a mixture of 37% aqueous hydrochloric acid and water. The solutions

contain, respectively, 0.0005 grams and 2.5 grams of palladium per liter.

EXAMPLE 7

The concentrates of Example 5 are diluted with enough 1:1 mixture by volume of 37% hydrochloric acid and water to provide sensitizing solutions according to this invention containing, respectively, 0.001, 1.0 and 2.5 grams/liter of ruthenium, rhodium, osmium, iridium and platinum.

The stannous fluoborate, stannous sulfate and acetic acid containing sensitizing solutions are made up in a manner similar to that described hereinabove.

The sensitizing process of this invention comprises the steps of cleaning the panel surfaces including any side walls of apertures defined therein, immersing the panel in the diluted solution containing, preferably, from 0.0005 to 2.5 grams/liter precious metal in the form of the complex of this invention, and thereafter thoroughly rinsing the surface with water. The panel is then passed through a further bath solution consisting of hydrochloric acid, suitable diluted, e.g., to about 10% by volume, and is again rinsed with water prior to immersion in a suitable electroless plating bath.

WHAT WE CLAIM IS:—

1. A sensitizing solution for rendering a surface receptive for the electroless deposition of an adherent metal layer, which comprises a solution of a double metal complex consisting of three components:

(a) a precious metal selected from the metals of the fifth and sixth periods of Groups VIII and IB of the periodic table of elements;

(b) a Group IV metal of the periodic table of elements which is capable of two valence states; and

(c) an anion capable of forming a stable moiety with both valence states of the Group IV metal,

the molar ratio of components (a) to (b) being 1:1:3 to 1:6:24; the said double metal complex having been formed by heating an aqueous mixture containing said components (a), (b) and (c) for a period of time which is sufficient for its formation.

2. A stable concentrated composition, dilutable to an optically clear, sensitizing solution for rendering a surface receptive for the electroless deposition of an electrolessly formed metal deposit which comprises water and a double metal complex consisting of

(a) a precious metal selected from the group consisting of the precious metals of the fifth and sixth periods of Groups VIII and IB of the periodic table of elements;

(b) a Group IV metal of the periodic table

of elements which is capable of two valence states; and

(c) an anion capable of forming a stable moiety with both valence states of the Group IV metal,

the molar ratio of components (a) to (b) to (c) being at least 1:1:3 and wherein the concentration of component (a) is at least .5 grams/liter; the said double metal complex having been formed by heating an aqueous mixture containing said components (a) and (b) and (c) for a period of time which is sufficient for forming said complex.

3. The solution as defined in Claim 1 or Claim 2 which further includes an excess of component (b) and of component (c).

4. An optical clear sensitizing solution for rendering a surface receptive to the electroless deposition of an adherent metal coating which has been prepared by diluting the concentrated composition of Claim 2 with water, and an acid, or a mixture thereof, until the concentration of component (a) has been reduced to from 0.0005 grams/liter to 0.5 grams/liter.

5. The solution as claimed in one of the claims 1 to 4 wherein component (c) is Cl^- , SnCl_4^- or a mixture thereof.

6. The solution as claimed in one of the preceding claims, said metal complex includes an anion of the formula:



or a mixture thereof, wherein Me is a metal selected from the fifth and sixth period of Group VIII and IB of the periodic table of elements or a mixture thereof.

7. The solution as claimed in at least one of the preceding claims which comprises a stabilizer, selected from the group of organic mono-ols, di-ols and poly-ols, the amount of said organic compound present in said solution being at least sufficient to prevent separation therefrom of component (a) as a metallic film or as particles or as a precipitate.

8. The solution of Claim 7 wherein the stabilizer has a relatively low molecular weight and is polysubstituted with hydroxy groups or with at least one hydroxy group and other functional groups such as sulfonic acid groups, phosphate groups, amino groups, halogens and carboxyl groups.

9. The solution as claimed in Claim 1 or 5 wherein the solvent is an organic solvent.

10. The solution as claimed in Claim 9 wherein the organic solvent is selected from dimethylformamide, cyclohexanone, hexane, dimethyl sulfoxide.

11. A process for the preparation of a concentrated composition as defined in Claim 2 which comprises heating an aqueous mixture containing components (a), (b) and (c) for a period of time which is sufficient for substantially all of component (a) to react with components (b) and (c) and to form a double metal complex. 25
12. A process for the preparation of a concentrated composition as defined in Claim 2 which comprises 30
- (1) providing an aqueous solution containing a water soluble salt of said component (a) in a concentration of from 1.5 grams/liter up to the limit of solubility of said salt in water; and component (c); 35
- (2) providing an aqueous solution of said components (b) and (c), the ratio of components (a):(b):(c) being 1 to at least 1 to at least 3; and 40
- (3) mixing said solutions and heating the mixture for a period of time sufficient for substantially all of component (a) to form with components (b) and (c) a double metal complex.
13. The process of Claim 11 or of Claim 12 wherein the mixture is heated to the temperature of its boiling point.
14. The process of one of the Claims 11 to 13 wherein the mixture is first heated to a temperature below the boiling point, preferably to 80° to 85°C.
15. A process for electrolessly plating an adherent metal deposit on a substrate which comprises sensitizing said substrate by contacting same with a sensitizing solution as defined in one or more of the claims 1 to 9, substantially removing the said sensitizing solution by rinsing said substrate with water, and then contacting said bath with and electroless metal plating bath and electrolessly depositing metal on said sensitized substrate.

For and on behalf of
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